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Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):

Fock, J., Bogart, L. K., Posth, O., Hansen, M. F., Pankhurst, Q. A., & Frandsen, C. (2015). *Uncertainty budget for determinations of mean isomer shift from Mössbauer spectra*. Poster session presented at The International Conference on the Applications of the Mössbauer Effect , Hamburg, Germany.

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Uncertainty budget for determinations of mean isomer shift from Mössbauer spectra



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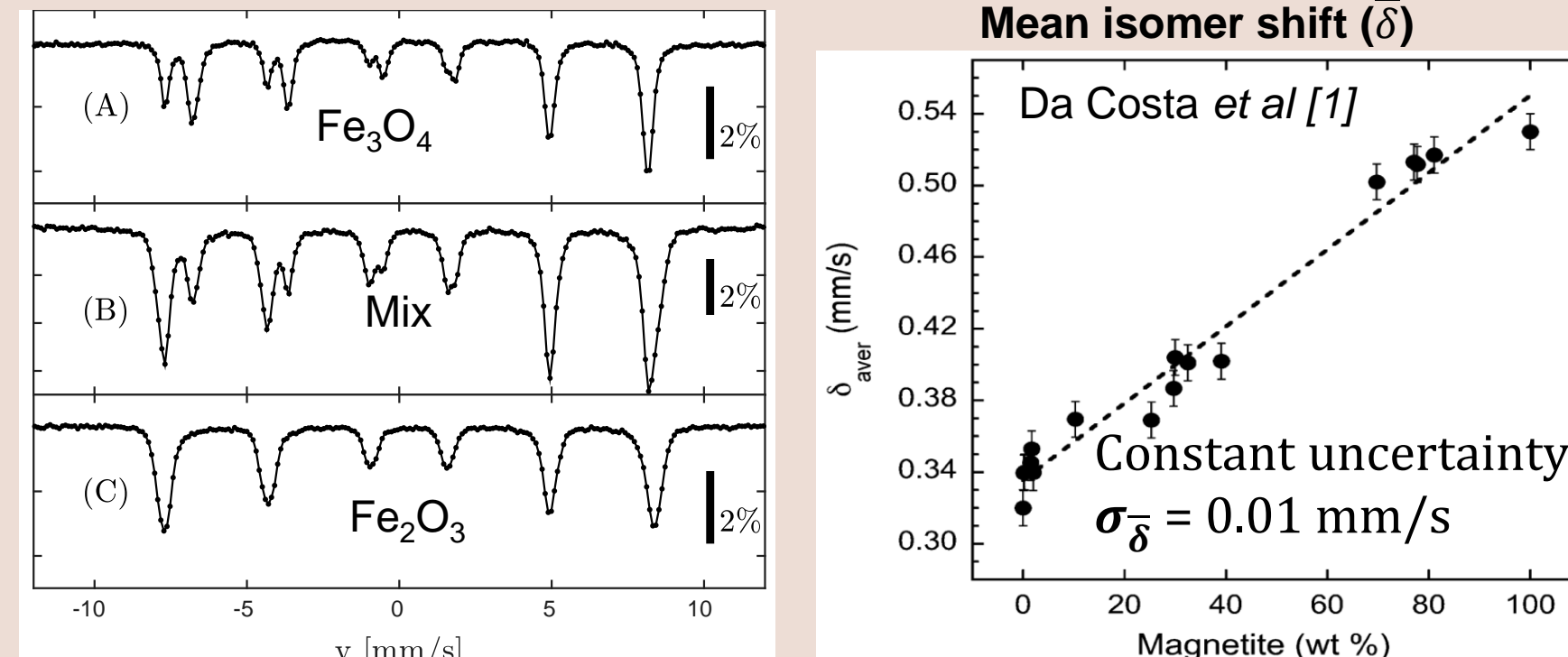
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Introduction and Motivation

Mössbauer spectroscopy is one of the few methods which is able to distinguish between magnetite (Fe₃O₄) and maghemite (Fe₂O₃), eg.

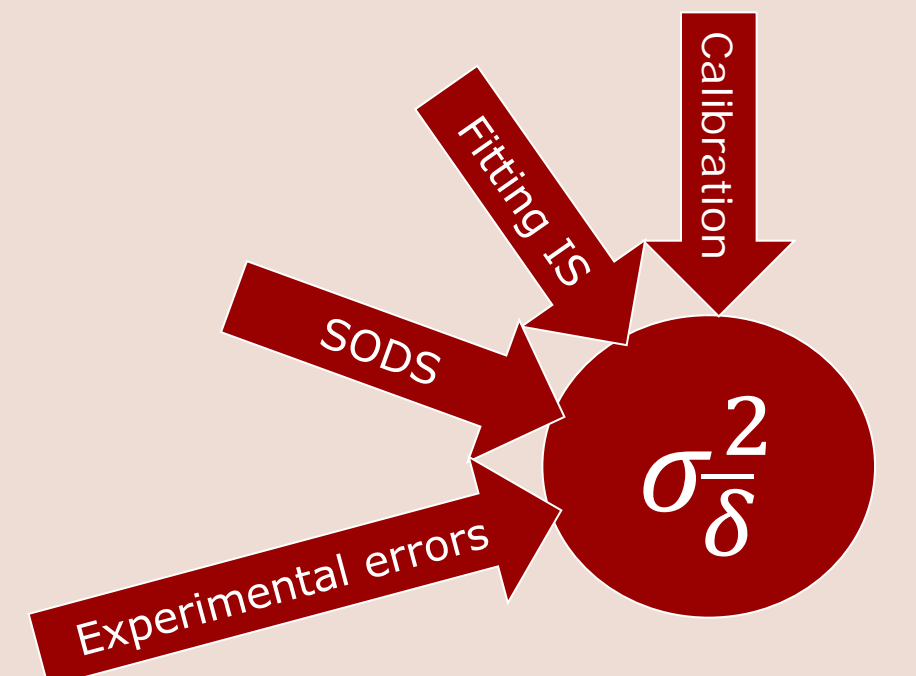
1. The presence or absence of characteristic lines
2. Area ratio of spectral components
3. Mean isomer shift ($\bar{\delta} = \sum_n A_n \delta_n / A$)



The uncertainty of the mean isomer shift ($\sigma_{\bar{\delta}}$) can be divided up into four uncorrelated contributions:

- 1) The calibration (σ_{cal}),
- 2) Correction of Second order Doppler shift ($\sigma_{\Delta\delta}$)
- 3) The fitting of the spectrum (σ_{fit}),
- 4) Experimental errors (σ_{err}).

$$\sigma_{\bar{\delta}}^2 = \sigma_{cal}^2 + \sigma_{fit}^2 + \sigma_{\Delta\delta}^2 + \sigma_{err}^2$$



1. Calibration, σ_{cal}

Channel-velocity calibration is performed by fitting

$$c_n = \frac{E_n}{k} + c_0 \quad \text{for } 1 \leq n \leq 6$$

$$c_n = \frac{-E_{13-n}}{k} + c_0 + \frac{c_f}{2} \quad \text{for } 7 \leq n \leq 12$$

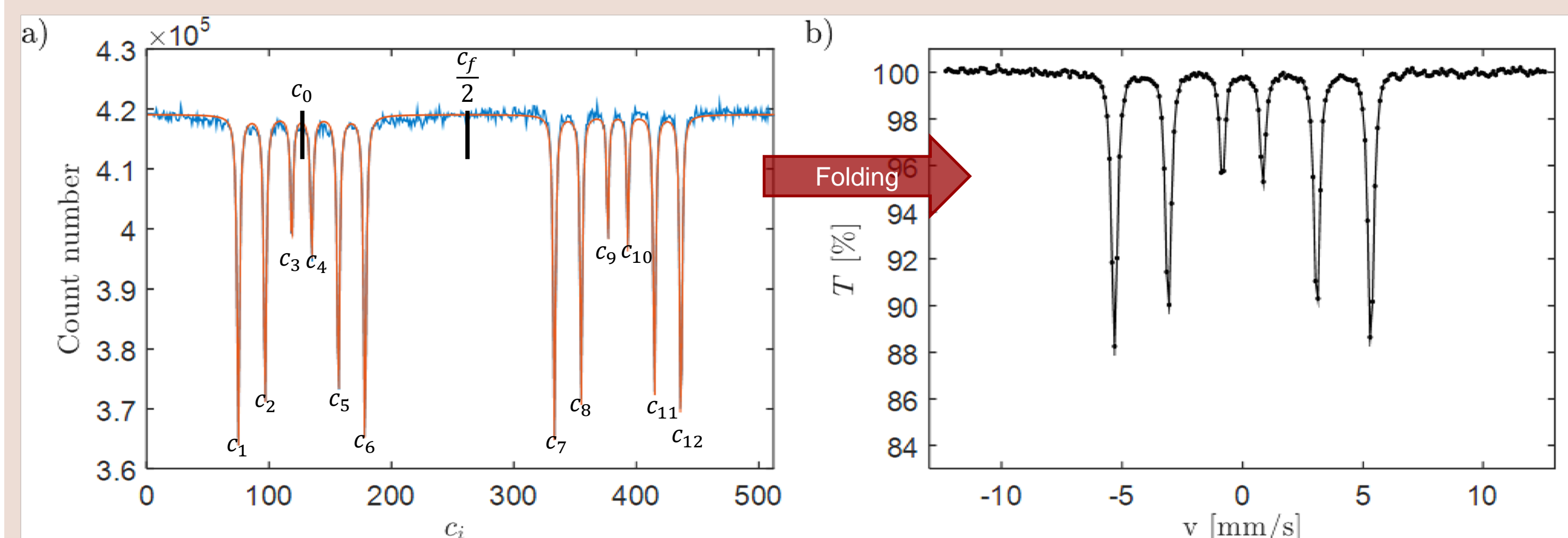
to all twelve peaks in the unfolded α -Fe foil reference spectrum (fig 1a) using the energy of n th line in the reference spectrum (E_n).

From the linear regression the covariance matrix is obtained:

$$\Sigma_{c_0,k} = \begin{bmatrix} \sigma_{c_0}^2 & \sigma_{c_0,k} \\ \sigma_{c_0,k} & \sigma_k^2 \end{bmatrix}$$

Uncertainty in the isomer shift is:

$$\sigma_{cal} = \sqrt{\frac{\delta^2}{k^2} \cdot \sigma_k^2 + k^2 \cdot \sigma_{c_0}^2 - 2k\delta \sigma_{k,c_0}}$$



Results

- $\Sigma_{c_0,k} = \begin{bmatrix} 1.3 \cdot 10^{-3} & 2.7 \cdot 10^{-23} \\ 2.7 \cdot 10^{-23} & 2.8 \cdot 10^{-10} \end{bmatrix}$
- Uncertainty for $\bar{\delta} = 0$ is $\sigma_{cal} = 0.0017$ mm/s.

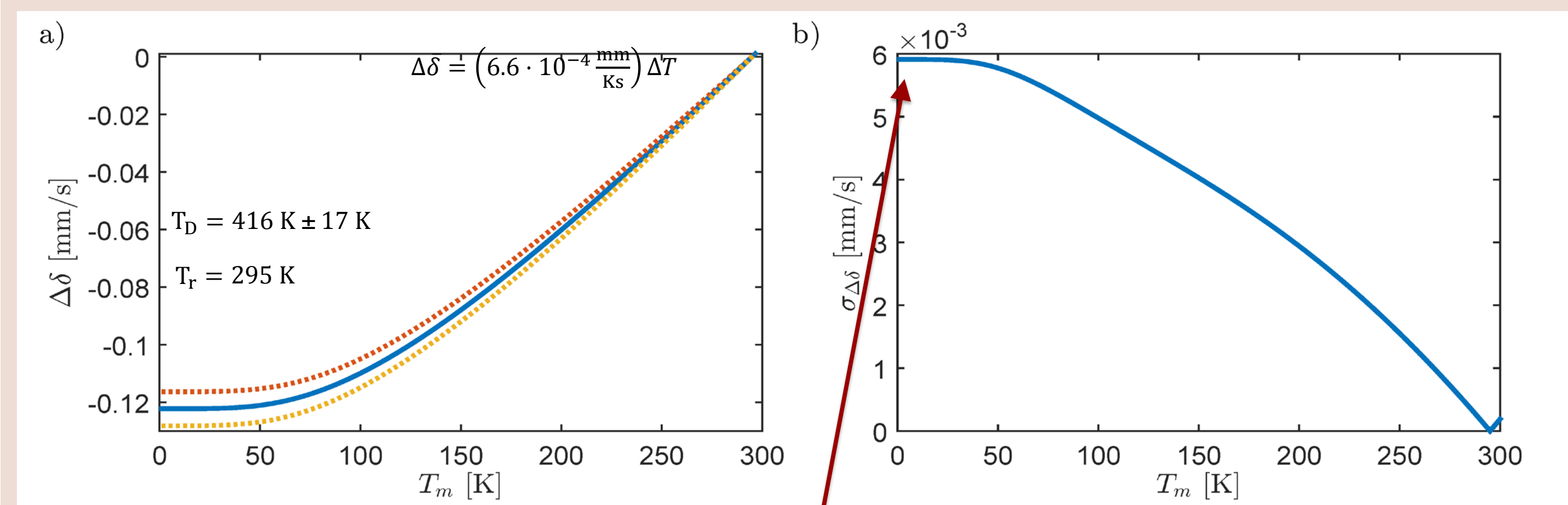
2. Correction for SODS

When the sample is measured at temperature (T_m) different from the temperature of reference compounds (T_r), the second order Doppler shift (SODS) describe the correction needed ($\Delta\delta$):

$$\Delta\delta = \frac{-9k_B}{2mc} \left[T_r \left(\frac{T_r}{T_D} \right)^3 \int_0^{T_D/T_r} \frac{x^3}{e^x - 1} dx - T_m \left(\frac{T_m}{T_D} \right)^3 \int_0^{T_D/T_m} \frac{x^3}{e^x - 1} dx \right]$$

The uncertainty is calculated using propagation of uncertainty:

$$\sigma_{\Delta\delta} = \left| \frac{\partial \Delta\delta}{\partial T_D} \right| \sigma_{T_D} = \left| 3 \frac{\Delta\delta}{T_D} + \frac{9k_B}{2mc} \left(\frac{1}{e^{T_D/T_r} - 1} - \frac{1}{e^{T_D/T_m} - 1} \right) \right| \sigma_{T_D}$$



- The SODS correction adds an uncertainty of up to 0.006 mm/s to the total uncertainty of $\bar{\delta}$.

- At high temperatures the mean isomer correction is approximately linear.

- Uncertainty in the temperature (σ_T).
- Seasonal or day/night temperature changes can induce uncertainties in $\bar{\delta}$

3. Fitting of spectrum, σ_{fit}

1. Spectrum S_i fitted to model $f(v_i, \mathbf{p})$ by minimizing:

$$\chi^2 = \sum_i (f_i(\mathbf{p}))^2 \quad \text{where } f_i(\mathbf{p}) = \frac{S_i - f(v_i, \mathbf{p})}{\sigma_{S_i}}$$

Fitted parameters (\mathbf{p}) consist of the areas (A_n) and isomer shifts (δ_n) of the N spectral components.

2. The covariance matrix of fitting parameters:

$$\Sigma_{\mathbf{p}} = (J(\mathbf{p})^T J(\mathbf{p}))^{-1}, \quad J(\mathbf{p}) = \begin{bmatrix} \frac{\partial f_1(\mathbf{p})}{\partial A_1} & \dots & \frac{\partial f_1(\mathbf{p})}{\partial \delta_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_N(\mathbf{p})}{\partial A_1} & \dots & \frac{\partial f_N(\mathbf{p})}{\partial \delta_N} \end{bmatrix}$$

3. Uncertainty of mean isomer shift is calculated by propagation of uncertainties:

$$\sigma_{fit}^2 = J_{\bar{\delta}} \Sigma_{\mathbf{p}} J_{\bar{\delta}}^T$$
$$J_{\bar{\delta}} = \begin{bmatrix} \frac{\partial \bar{\delta}}{\partial A_1} & \dots & \frac{\partial \bar{\delta}}{\partial A_N} & \frac{\partial \bar{\delta}}{\partial \delta_1} & \dots & \frac{\partial \bar{\delta}}{\partial \delta_N} \end{bmatrix}$$
$$= \begin{bmatrix} \frac{\delta_1 - \bar{\delta}}{A} & \dots & \frac{\delta_N - \bar{\delta}}{A} & \frac{A_1}{A} & \dots & \frac{A_N}{A} \end{bmatrix}$$

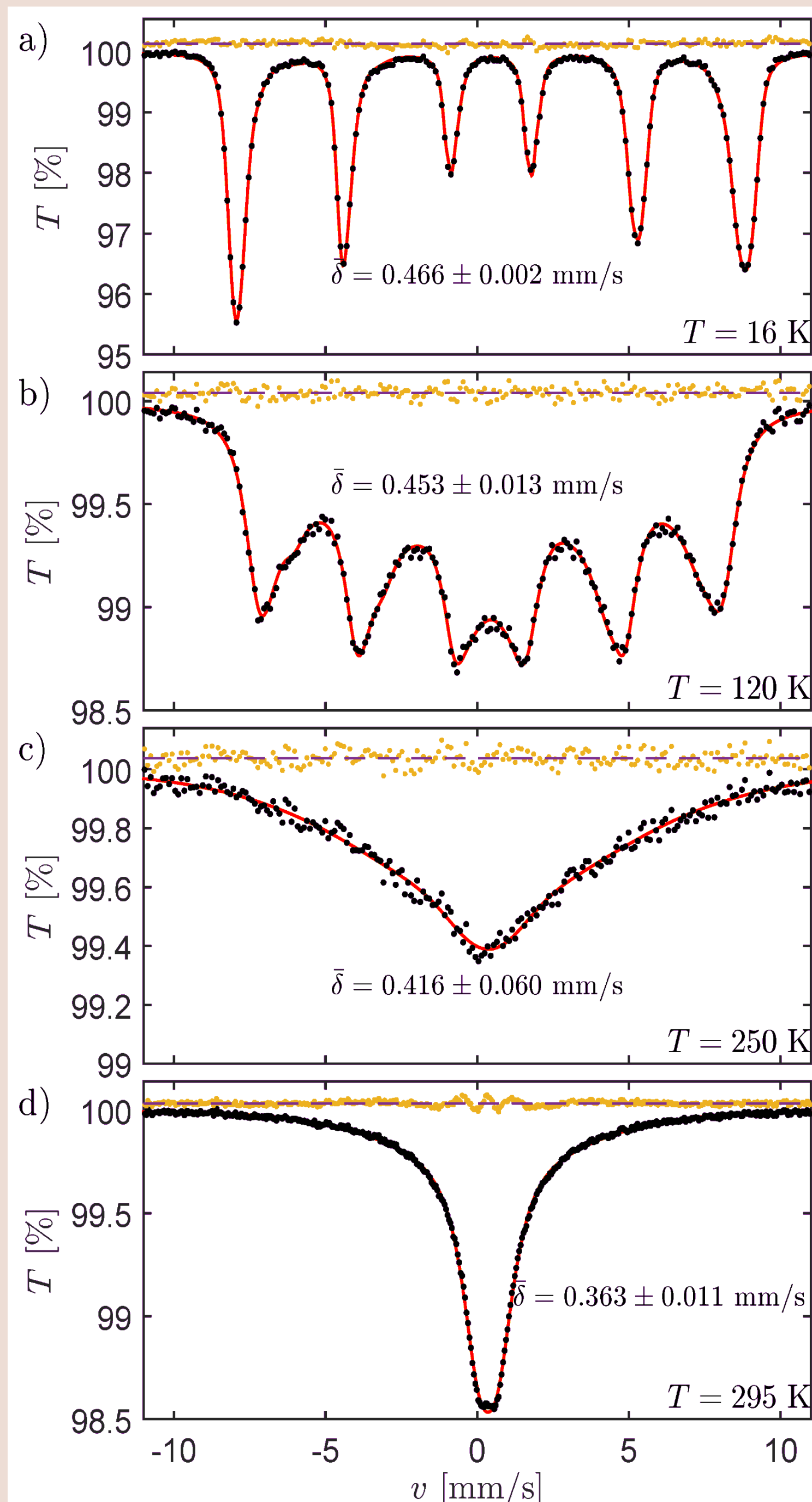
Results

a) Uncertainty of individual components is larger than 0.006 mm/s. Inducing correlations between parameters the uncertainty on $\bar{\delta}$ is 0.002 mm/s.

b-c) Broadening of spectra increase uncertainty.

d) Collapse into the doublet decreases uncertainty.

Multi-core, polystyrene iron oxide nanoparticles. Nominal size 8 nm



4. Discussion and Conclusion

- The experimental error (σ_{err}) is difficult to quantify.

- It is important to have:

- A flat non-sloping background
- Sufficient counting statistics.

Dominated by SODS correction Magnetite content						
T [K]	σ_{cal} [mm/s]	σ_{fit} [mm/s]	$\sigma_{\Delta\delta}$ [mm/s]	$\sigma_{\bar{\delta}}$ [mm/s]	w [%]	
16	0.0015	0.0015	0.0059	0.0063	4 ± 1	
120	0.0015	0.013	0.0046	0.014	7 ± 6	
250	0.0015	0.0596	0.0016	0.060	24 ± 28	High uncertainty due to: <ul style="list-style-type: none">• Broad lines• Low recoil-free fraction
295	0.0016	0.0108	0	0.011	13 ± 5	

Insufficient

Dominated by fitting uncertainty

The values are not equal within the uncertainty budget:

- Uncertainty in temperature not included.
- Possible experimental errors

Conclusion

- The uncertainty is not constant
- The fit introduce uncertainties
 - Spectrum with narrow lines gives low uncertainty
- Uncertainty in calibration is insignificant
- Correcting using SODS can result in a significant uncertainty
- Temperature uncertainty introduces uncertainty in mean isomer shift

Acknowledgements

We thank Abhilash Sugunan, Jens Sommertune and Andrea Fornara at the SP Technical Research Institute of Sweden for providing the nanoparticle sample. This work is financially supported by the EU FP7 Grant No. 604448-NanoMag.

